# Numerical surface treatment for finite-extent semiconductor nanostructures

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***Abstract*** – *The physics of nano-scale devices is largely influenced by interfaces and boundaries. Of particular interest is the numerical treatment of the boundary of finite-extent devices. Within the empirical tight-binding model, two kinds of boundary conditions are examined; (i) raising the orbital energies of surface atoms, (ii) raising the energies of dangling bonds at the surface. The Lanczos algorithm is used to obtain the eigenvalues of the tight-binding Hamiltonian. The orbital-energy shift leads to the slow convergence of conduction electron states above the gap and many surface states in the middle of the gap. In contrast, the dangling-bond energy shift leads to the fast convergence of the full spectrum of electronic structures, and efficiently eliminates all nonphysical surface states in the middle of the gap. The remaining spectrum of the electronic structure is insensitive to the change of the energy shift.*

**Keywords:** Boundary condition, electronic structure, empirical tight-binding model, Lanczos algorithm, semiconductor nanostructure.

## 1. INTRODUCTION

The empirical tight-binding model has been successful in efficiently describing the electro-magnetic and optical properties of semiconductor nanostructures [1-8]. The success results from the flexibility of determining the tight-binding Hamiltonian and overlap parameters and the minimization of the number of basis orbitals with atomic orbitals of valence electrons [9-12]. Compared to other atomistic models such as the pseudo-potential and density-functional theory, the tight-binding model is computationally efficient due to the minimized number of basis orbitals [13-16]. However, even with the efficient tight-binding model, the calculation of the electronic structure of nanostructures is still computationally challenging because the number of atoms involved in the nano-system can reach over 10 millions.

The majority of atoms in nanostructures constitutes a buffer layer which surrounds a core nanostructure such as a quantum dot, wire, and well. The buffer layer usually provides a confining potential to the electron Hamiltonian. The potential leads to bound electron states that are effectively confined in the core nanostructure. The leakage of the electron states to the buffer layer exponentially decreases with increasing the distance from the core nanostructure. Therefore, it is not necessary to model the buffer layer with a real size which can be as large as 100 nm. In determining the size of the modeled buffer layer, there is a trade-off between computational efficiency and accuracy. This leads to the need of finding a sensible boundary condition that can efficiently imitate a large buffer layer with a relatively small buffer. The sensible boundary condition should efficiently eliminate all nonphysical surface states, and at the same time minimally affect physical interior states. In this work, we examine two kinds of boundary conditions to find an efficient and reliable treatment. The efficiency and reliability are measured by the required Lanczos iteration number for eigenvalue convergence and the elimination of nonphysical surface states.

## 2. BOUNDARY CONDITIONS

The first boundary condition considered is to raise the orbital energies of surface atoms. This method discourages electrons from populating the surface-atom orbitals. However, this treatment does not differentiate surface atoms with a different number of dangling bonds, which ranges from one to three in zinc-blende crystal structures. Therefore, we also consider the second boundary condition that is to raise the dangling-bond energies of surface atoms. Within this method, the connected-bond energy of surface atoms is intact and hence there is no extra penalty for electrons to occupy the connected bonds of surface atoms. When the modeled buffer layer is large enough, both boundary conditions should in principle yield an almost identical electronic structure since the effect of surface atom is small in the large buffer.

Within the boundary condition I of raising orbital energies, the Hamiltonian block matrix for a surface atom with basis set {|s>, |p$_x$>, |p$_y$>, |p$_z$>, |s*>} is given by

$$\begin{pmatrix} E_s + \Delta_s & 0 & 0 & 0 & 0 \\ 0 & E_p + \Delta_p & 0 & 0 & 0 \\ 0 & 0 & E_p + \Delta_p & 0 & 0 \\ 0 & 0 & 0 & E_p + \Delta_p & 0 \\ 0 & 0 & 0 & 0 & E_{s*} + \Delta_{s*} \end{pmatrix}, (1)$$

where $E$ is the energy of the basis orbital and $\Delta$ is the energy shift for the orbital on a surface atom. A

different energy shift can be chosen for a different basis orbital.

For the boundary condition II of raising dangling-bond energies, we first change the basis set of the Hamiltonian block matrix from $\{|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle, |s^*\rangle\}$ to the set of hybridized orbitals that are aligned along bond directions. In the zinc-blende structure, the hybridized orbitals are

$$|sp^a\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle),$$

$$|sp^b\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle),$$

$$|sp^c\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle),$$ (2)

$$|sp^d\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle).$$

Second, we raise the energy of a hybridized orbital by $\Delta_{sp}$ if the orbital is along the dangling bond direction. For instance, if the surface atom has two dangling bonds along $|sp^a\rangle$ and $|sp^c\rangle$ directions, the Hamiltonian block matrix for the surface atom is given by

$$\begin{pmatrix} A + \Delta_{sp} & B & B & B & 0 \\ B & A & B & B & 0 \\ B & B & A + \Delta_{sp} & B & 0 \\ B & B & B & A & 0 \\ 0 & 0 & 0 & 0 & E_{s^*} \end{pmatrix},$$ (3)

where $A = E_s/4 + 3E_p/4$ and $B = E_s/4 - E_p/4$.

Finally, we transform the Hamiltonian back into the original basis set of $\{|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle, |s^*\rangle\}$. The final Hamiltonian block matrix of the surface atom becomes

$$\begin{pmatrix} E_s + \frac{\Delta_{sp}}{2} & 0 & \frac{\Delta_{sp}}{2} & 0 & 0 \\ 0 & E_p + \frac{\Delta_{sp}}{2} & 0 & \frac{\Delta_{sp}}{2} & 0 \\ \frac{\Delta_{sp}}{2} & 0 & E_p + \frac{\Delta_{sp}}{2} & 0 & 0 \\ 0 & \frac{\Delta_{sp}}{2} & 0 & E_p + \frac{\Delta_{sp}}{2} & 0 \\ 0 & 0 & 0 & 0 & E_{s^*} \end{pmatrix}.$$ (4)

In comparison with Eq. (2), this block matrix contains nonzero off-diagonal elements. Furthermore, the shift of the diagonal element is proportional to the number of dangling bonds. If the surface atom has $n$ dangling bonds, the energy shift of the diagonal element is given by $n\Delta_{sp}/4$. Therefore, this boundary condition distinguishes surface atoms with a different number of dangling bonds.

In some degree, the boundary condition II mimics the physical passivation of dangling bonds with other atoms such as hydrogen and oxygen. Experimentally, silicon surfaces are usually passivated by hydrogens to improve the conductivity. The hydrogens form bonding and anti-bonding states with the dangling bonds of Si at the surface. For example, the energies of the bonding and anti-bonding states of SiH$_4$ are about 18 eV and 5 eV below the valence band edge of bulk Si, respectively [17]. Therefore, hydrogen

passivation efficiently removes surface states localized in dangling bonds. In connection with this mechanism, the boundary condition II can be seen as forming the bonding/antibonding state between a dangling bond and "vacuum" at the energy determined by $\Delta_{sp}$.

## 3. RESULTS

We choose a self-assembled InAs quantum dot to test the two types of boundary conditions. The self-assembled dot is surrounded by a GaAs buffer layer. The dot is lens shaped with diameter 30 nm and height 6 nm. The dot is composed of 113,347 atoms. An appropriate size for the GaAs buffer layer depends on the type of calculations. For strain-profile calculations, the buffer thickness should be as large as the dot size since the strain effect is long-ranged [18]. For electronic-structure calculations, the buffer thickness can be smaller than the dot size because bound electron states are effectively spatially confined inside the dot. Therefore, we use the buffer-layer thickness 20 nm for strain-profile calculations, and reduce the thickness to 5 nm for the electronic-structure calculation while keeping the atomic positions obtained from the strain calculation. The equilibrium atomic positions are calculated by minimizing the strain energy using Keating's atomistic valence-force-field model [19][20].

The tight-binding Hamiltonian for the InAs dot and the GaAs buffer is constructed based on $sp^3d^5s^*$ orbitals and up to nearest-neighbor interactions. The parameters are chosen by fitting them to bulk band structures with a genetic algorithm [20]. To take into account the effect of the displacements of atoms from unstrained crystal structures, the atomic energies (the diagonal parts of the tight-binding Hamiltonian) are adjusted by a linear correction within the Löwdin orthogonalization procedure [21][22]. The coupling parameters between nearest-neighbor orbitals (the off-diagonal parts of the tight-binding Hamiltonian) are also modified according to the generalized Harrison's $d^{-2}$ scaling law and Slater-Koster direction-cosine rules [23][24].

Implementing the two boundary conditions requires a sensible choice of the energy shift $\Delta$ for surface atoms. The energy shift should be high enough to discourage electrons from occupying the surface atom orbitals and consequently to eliminate all nonphysical surface states. At the same time, it should be small enough to minimally affect the electronic structure of interior states. The diagonal energies of the tight-binding Hamiltonian gives a guide to the energy shift. The diagonal energies are ranged from –0.6 eV to 20 eV. Therefore, we choose the energy shift on the order of the tight-binding Hamiltonian parameters. The energy shifts used in this calculation are $\Delta_s = 5$ eV, $\Delta_p = 4$ eV, $\Delta_d = 3$ eV, $\Delta_{s^*} = 0$ eV, and $\Delta_{sp} = 10$ eV. The effect of the energy shift on the electronic structure is discussed in detail later in the paper.

Lanczos algorithm is used to obtain the eigenvalues of the tight-binding Hamiltonian [25]. Lanczos algorithm is the most commonly used iterative eigenvalue solver for a large-dimensional,

sparse, hermitian matrix, which is the case for the tight-binding Hamiltonian. At each Lanczos iteration, the large matrix is projected into a lower-dimensional subspace. The reduced matrix is tridiagonal and its eigenvalues approximate those of the original large matrix when the eigenvalues converge.

Figure 1 presents the eigenvalues of the Lanczos tridiagonal matrix as a function of the number of Lanczos iterations. The boundary condition II of raising dangling-bond energies leads to the fast convergence of the full spectrum of eigenvalues, while the boundary condition I of raising orbital energies of surface atoms yields the slow convergence of only the partial spectrum. To visualize the importance of having a proper boundary condition, the eigenvalues without boundary condition are also plotted in Figure 1(c). When no boundary condition is implemented, many surface states are formed, and it prevents Lanczos algorithm from resolving eigenvalues for physical interior states.
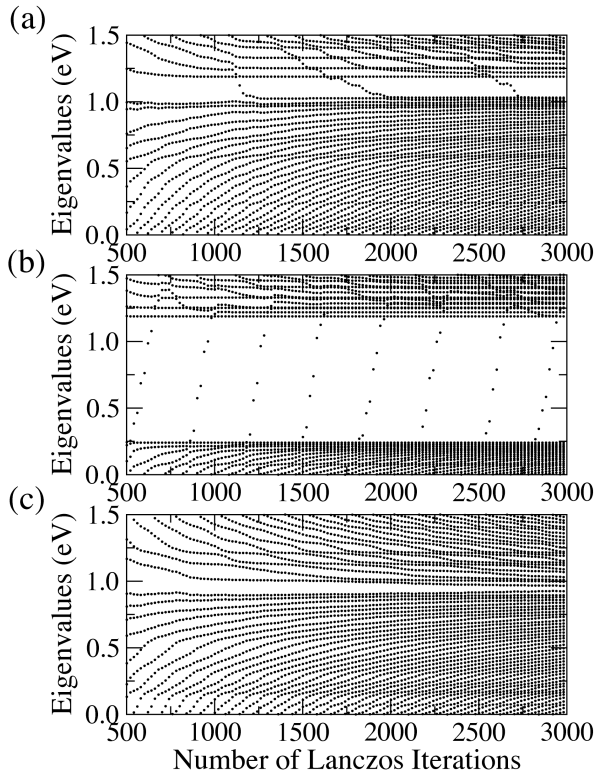


Figure 1: Eigenvalues of the Lanczos tridiagonal matrix versus the number of Lanczos iterations (a) with the boundary condition I of raising surface-atom-orbital energies, (b) with the boundary condition II of raising dangling-bond energies, and (c) without boundary condition.

The boundary condition II efficiently eliminates all nonphysical surface states in the middle of the gap between about 0.3 eV and 1.2 eV, as shown in Figure 1(b). In contrast, the boundary condition I leads to many surface states in the middle of the gap (see Figure 1(a)). The dense spectrum of nonphysical surface states prevents the convergence of bound hole states below 0.3 eV. These qualitatively different spectra between the boundary conditions I and II show that it is essential in modeling the electronic structure

to use the boundary condition that can efficiently eliminate all nonphysical surface states.

In terms of the number of Lanczos iterations required to obtain the converged eigenvalues, the boundary condition II is also more efficient than the boundary condition I. Table I lists the number of Lanczos iterations required for a given number of converged eigenvalues for both boundary conditions. For example, to acquire four eigenvalues, the boundary condition I requires twice as many iterations as the boundary condition II. The efficiency of the boundary condition II is attributed to the elimination of the dense spectrum of surface states. In general, iterative eigenvalue solvers easily find eigenvalues in a sparse spectrum, but show difficulty resolving eigenvalues in a dense spectrum.

Table I: Number of Lanczos iterations required to obtain converged eigenvalues for the boundary condition I of raising orbital energies of surface atoms and for the boundary condition II of raising dangling-bond energies.

| Number of converged eigenvalues | Boundary condition I | Boundary condition II |
|---|---|---|
| 1 | 1460 | 520 |
| 2 | 3740 | 1280 |
| 3 | 3860 | 1860 |
| 4 | 4600 | 2040 |

Finally, we investigate the reasonable choice of the energy shift $\Delta_{sp}$ for the boundary condition II. The ultimate goal is to eliminate any surface states and at the same time to minimally affect the electronic structure of interior states. Figure 2 shows converged eigenvalues with respect to energy shift $\Delta_{sp}$. Energy shift $\Delta_{sp}=5$ eV leads to many surface states in the middle of the gap. However, when the energy shift is higher than 10 eV, all the surface states are eliminated and the converged eigenvalues vary only within 0.1 meV. This indicates that the electronic structure is insensitive to the choice of the energy shift within the boundary condition II if the shift is big enough to remove all surface states. In contrast, the effect of the choice of energy shifts in the boundary condition is highly unpredictable as the slight change of shifts leads to completely different Lanczos eigenvalue spectrum. For instance, changing $\Delta_p$ from 4 eV to 5 eV leads to no converged eigenvalues even above 1.3 eV, in comparison with Figure 1(a).
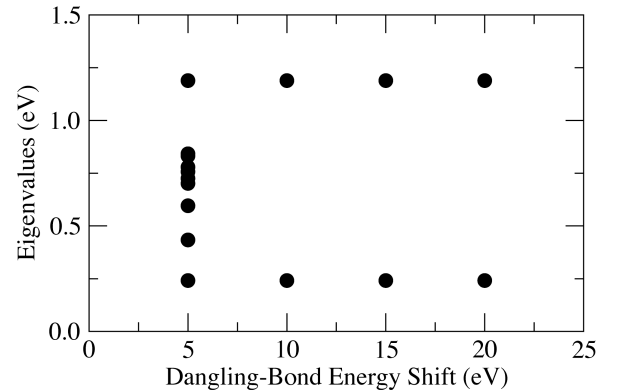


Figure 2: Converged eigenvalues of Lanczos tridiagonal matrix versus dangling-bond energy shift.

## 4. CONCLUSION

In summary, we have investigated the two types of boundary conditions for the electronic structure of semiconductor nanostructures with empirical tight-binding model. The boundary condition II of raising dangling-bond energies demonstrates higher efficiency than the boundary condition I of raising orbital energies of surface atoms, in terms of both surface-state elimination and eigenvalue-convergence speed. With the efficient boundary condition II, we have further examined the effect of the dangling-bond energy shift on the electronic structure. The energy shift bigger than about 10 eV efficiently removes all nonphysical surface states in the middle of the gap, and yields the energy gap highly insensitive to the change of the energy shift.

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